

(19)

Europäisches Patentamt
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(11) **EP 0 474 376 B1**

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
01.05.1996 Bulletin 1996/18

(51) Int Cl. 6: **C08L 23/10, C08L 23/08,
C08J 5/18, B32B 27/32**

(21) Application number: **91307438.1**

(22) Date of filing: **13.08.1991**

(54) Films of blends of polypropylene and ethylene copolymer

Filme aus Polypropen- und Äthencopolymermischungen

Films de mélanges de polypropène et copolymère d'éthène

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

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(30) Priority: **13.08.1990 US 566594
22.02.1991 US 659215**

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(43) Date of publication of application:
11.03.1992 Bulletin 1992/11

(56) References cited:

(60) Divisional application: **95115424.4**

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Description

The present invention pertains to packaging films, and more particularly to a thin polymeric film suitable for replacing polyvinyl chloride film especially in packaging applications.

5 Polyvinyl chloride (PVC) has long been used in many applications in the packaging art. One particularly widespread application for PVC is the use of such material as an overwrap material for trayed retail cuts of meat and other food products in a retail environment such as a supermarket.

PVC has several desirable properties for this use. For example, it has excellent burn-through resistance, optics and good elasticity and stretch properties at use temperatures.

10 Unfortunately, PVC also has several disadvantages, including the production of hydrogen chloride gas during heat sealing and the generally corrosive effects of such gases in the packaging room. Extractables from the PVC into the packaged food product have also become of concern.

It would be of great benefit to the packaging industry, and particular to applications requiring an instore film for 15 overwrapping trayed food products, to provide a film with many of the advantages of PVC but without the disadvantages described above.

The inventors have discovered that a blend of propylene polymer or copolymer, and ethylene copolymer, is useful in improving the burn-through resistance of a film made from the blend.

The inventors have also discovered that a relatively thin polymeric film, including a layer of the blend combined with an outer heat sealable layer, can be made using the inventive blend.

20 Processes for producing oriented films, and oriented films themselves are disclosed in many patents including the following patents of interest.

U. S. Patent No. 3,456,044 and U. S. Patent No. 3,555,604 (Pahlke) mentions thin films of thicknesses less than 1 mil such as 0.5 mils, and discloses a double bubble method for biaxially orienting thermoplastic films including the steps of producing a primary tubing which is inflated by introducing air into the interior thereof, and a cooling ring 22, 25 as well as squeeze rolls 34 and 28, with rolls 34 having a greater speed than rolls 28. Between the two pairs of squeeze rolls is a reinflated secondary bubble. If annealing is desired, the tubing can be reinflated to form a bubble 70.

U. S. Patent No. 4,258,166 (Canterino et al) discloses a uniaxially oriented plastic film material with improved strength and clarity in the direction of orientation preferably comprising homopolymers and copolymers of ethylene.

30 U. S. Patent No. 4,355,076 (Gash) discloses monoaxially oriented polypropylene film laminated to a monoaxially oriented high density polyethylene film, the films produced by for example tubular blowing.

U. S. Patent No. 4,440,824 (Bonis) discloses a thermoformable coextruded multilayer structure useful for thermo-forming into containers, the structure having polyolefin coextruded with a high impact polystyrene layer. A five layer structure is shown.

35 U. S. Patent No. 4,464,439 (Castelein) discloses a coextruded laminate having a sheet of polypropylene and a sheet of a mixture of high impact polystyrene, crystalline polypropylene, and styrene/dienic monomer block copolymer.

U. S. Patent No. 4,879,177 (Boice) discloses a monoaxially oriented shrink film having a core layer of butadiene styrene copolymer, outer layers of ethylene propylene copolymer, and intermediate bonding layers of ethylene copolymer.

40 Multi-layer packaging films have also been disclosed in EP-A- 0,144,642, US-A- 4,720,427, EP-A- 0,282,282, EP-A- 0,214,945, EP-A- 0,235,930, EP-A- 0,221,726 and US-A- 4,340,641.

It is an object of the present invention to provide a thermoplastic film useful as an overwrap material for trayed retail cuts of meat and other food products in a super market or other retail environment.

It is also an object of the present invention to provide a film which has good burn-through resistance.

45 It is also an object of the present invention to provide a film having excellent optical properties, specifically excellent gloss and clarity.

In one aspect the present invention provides a multilayer film comprising:

(a) a first layer comprising a blend of propylene homopolymer or copolymer, and very low density polyethylene, wherein the very low density polyethylene has a melt index before blending of no more than 10 grams/10 minutes measured according to ASTM D 1238 at condition 190/21.601, and a flow rate ratio ($I_{21}/I_{2,1}$) before blending of at least 40, said ratio being derived by dividing the flow rate at condition 190/21.6 by the flow rate at condition 190/2.16, measured according to ASTM D 1238, and

50 (b) an outer sealable layer.

55 In another aspect of the present invention, a method of making a polymeric film comprises coextruding a first melt stream of a blend of propylene polymer or copolymer, and very low density polyethylene wherein the very low density polyethylene has a melt index before blending of no more than 10 grams/10 minutes measured according to ASTM D 1238 at condition 190/21.601 and a flow rate ratio ($I_{21}/I_{2,1}$) before blending of at least 40, said ratio being derived by

dividing the flow rate at condition 190/21.6 by the flow rate at condition 190/2.16, measured according to ASTM D 1238, and a second melt stream of a sealable polymeric material; extruding the melt streams through a tubular die; hot blowing the extruded film; heating the hot blown film to a temperature above its orientation temperature; directing the heated film through a first set of pinch rolls; reinflating the hot blown film by a blown bubble process wherein the bubble is expanded in both its longitudinal and transverse directions; and collapsing the inflated film through a second set of pinch rolls.

The term "polyolefin" is used herein in its stricter sense to mean a thermoplastic polymer derived from simple olefins. Among these are polyethylene, polypropylene and copolymers thereof with olefinic comonomers. For example, very low density polyethylene may be considered a linear ethylene copolymer with a comonomer comprising such materials as butene, hexene or octene. The term "polyolefin" is also used herein in a broader sense to include copolymers of ethylene with comonomers that are not themselves olefins, such as vinyl acetate (e.g. ethylene vinyl acetate copolymer or EVA).

The term "very low density polyethylene", or "VLDPE" is used herein to describe linear ethylene alpha-olefin copolymer (flexomer) having densities of generally between 0.860 and 0.915 grams/cubic centimeter, and produced by a catalytic, low pressure process. "Ultra low density polyethylene" is also included in this term.

The term "ethylene vinyl acetate copolymer" (EVA) as used herein refers to a copolymer formed of ethylene and vinyl acetate monomers wherein the ethylene derived units are present in major amounts and the vinyl acetate derived units are present in minor amounts, preferably one (1) to thirty (30) percent by weight.

The term "styrene butadiene copolymer" (SBC) is used herein to denote thermoplastic copolymers, especially block copolymers containing a major portion (greater than 50%) of styrene and a minor proportion (less than 50%) of butadiene comonomer.

The terms "melt flow" and "melt index" are used herein to mean the amount, in grams, of a thermoplastic resin which is forced through an orifice of specified length and diameter in ten minutes under prescribed conditions in accordance with ASTM D 1238.

The term "flow rate ratio" (FRR) is used to mean a dimensionless number derived by dividing the flow rate (melt flow or melt index) at one Condition with the flow rate at another Condition (ASTM D 1238). FRR is indicative of molecular weight distribution. The higher the FRR, the broader the molecular weight distribution.

The term "ethylene copolymer" is used herein in its strict sense to mean copolymers of ethylene and a comonomer, and in its broad sense to include materials such as polybutene which can be substituted for this first group of materials.

The term "ethylene alpha olefin copolymer" is used herein to refer to copolymers of ethylene and higher alpha olefins such as butene, 1-methyl pentene, hexene, and octene.

The invention may be further understood by reference to the drawings herein, where:

FIG. 1 is a schematic cross section of a preferred embodiment of a multilayer film in accordance with the invention;

FIG. 2 is a schematic diagram indicating the apparatus and process by which the films of the present invention are made.

A preferred composition used in the film of the invention is a blend of between 20% and 80% propylene homopolymer or copolymer, and between 80% and 20% very low density polyethylene. A more preferred composition is a blend of from 30% to 70%, more probably 40% to 60% propylene homopolymer or copolymer, and from 30% to 70%, more preferably 40% to 60% very low density polyethylene. An even more preferred composition is a blend of about 50% propylene homopolymer or copolymer, and about 50% very low density polyethylene.

An especially preferred propylene resin is propylene ethylene copolymer such as that available from Fina under the designation Fina 8473 and Fina 8473x. These resins have an ethylene content of about 3% by weight.

Another especially preferred propylene resin is propylene homopolymer such as that available from Shell under the designation WRD5-981, with a melt flow rate of .6 to .8 grams/10 minutes (ASTM D 1238, Condition 230/2.16).

An especially preferred VLDPE is a high molecular weight resin such as DEFD 1015 from Union Carbide. This resin has a density of about .900 grams/cc, a melt flow-rate of about 6 grams/ 10 minutes (ASTM D 1238, Condition 190/21.601), and a FFR ($I_{21}/I_{2,1}$) of about 50.

The preferred film structure is a multilayer composite having a core layer 10 comprising a blend of propylene polymer or copolymer, and very low density polyethylene (VLDPE).

Preferred VLDPE resins are characterized by high molecular weight (i.e. relatively low melt index), broad molecular weight distribution (i.e. relatively high flow rate ratio), and relatively low crystallinity at processing temperatures.

For the VLDPE, a melt index (MI) of no more than about .15 grams/ 10 minutes (ASTM D 1238) (Condition 190/2.16) is preferred. A more preferred MI is .12 grams/ 10 minutes.

Preferred VLDPE resins can also be characterized by a melt index of no more than about .50 grams/ 10 minutes, more preferably no more than about .45 grams/ 10 minutes (ASTM D 1238) (Condition 190/5.0); no more than about

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1.50 grams/ 10 minutes, and more preferably no more than about 1.35 grams/ 10 minutes (ASTM D 1238) (Condition 190/10.); or no more than 10 grams/ 10 minutes, and more preferably no more than 6 grams/ 10 minutes (ASTM D 1238) (Condition 190/21.601).

For the VLDPE, a molecular weight distribution (flow rate ratio) of at least 10 (I_2/I_5) (ASTM D 1238) is preferred. 5 This value is derived by dividing the flow rate at Condition 190/21.6 by the flow rate at Condition 190/5.0. A more preferred FRR is 13.

VLDPE resins are also characterized by a FFR of at least 40, preferably at least 50 ($I_2/I_{2,1}$) (ASTM D 1238). This value is derived by dividing the flow rate at Condition 190/21.6 by the flow rate at Condition 190/2.16.

Referring to Fig. 1, in one preferred film construction, outer layers 12 preferably comprise a polyolefin, more preferably an ethylene polymer or copolymer such as EVA. Styrenic polymers and copolymers, e.g. styrene butadiene copolymer such as that commercially available from Phillips under the designation KR-10 having a butadiene content of 25% by weight of the copolymer, or KK 36 (for fatty food contact) are also preferred.

In this embodiment of the invention, the outer layers 12 are bonded to the core layer 10 by means of intermediate layers 14 each comprising a polymeric adhesive and preferably a copolymer of ethylene, and more preferably an ethylene vinyl acetate copolymer (EVA). A more preferred EVA is one having a vinyl acetate content above 18% by weight of the copolymer, and even more preferably 28% by weight of the copolymer. Other polymeric materials, including chemically modified adhesives, can be used for layers 14 provided they process adequately in processes such as those disclosed herein. Blends of polymeric materials and polymeric adhesives can also be used for intermediate layers 14.

20 For outer layers 12, SBC resins having minor amounts of butadiene, ranging from about 1 to 50%, provide an optimum balance of stiffness and flexibility to the film.

For layers of the present invention which contain SBC, antifog/plasticizing agents such as Atmer 645 and/or Atmer 1010 are preferably included, more preferably in amounts of between .5% and 10% by weight of the layer or layers. Even more preferably, between 2% and 6% of such agents are included. The intermediate layers 14, and comparable 25 layers in other films of the present invention, preferably also include such agents, more preferably in the .5% to 10% range.

The films of the present invention are preferably made by coextrusion techniques, combined with an apparatus and process depicted in Figure 2 and described in more detail below.

In one embodiment the film of the invention may comprise:

30 (a) a core layer comprising a blend of propylene homopolymer or copolymer and very low density polyethylene in accordance with the invention;
(b) two outer layers each comprising a sealable polymeric material; and
(c) two intermediate layers each bonding the core layer to a respective outer layer, and comprising a polymeric adhesive.

In a further embodiment the film of the invention may comprise:

40 (a) a core layer comprising a blend of propylene homopolymer or copolymer and very low density polyethylene in accordance with the invention;
(b) two interior layers, each layer bonded to an opposite side of the core layer, and comprising very low density polyethylene;
(c) two outer layers each comprising a sealable polymeric material; and
(d) two adhesive layers each bonding an interior layer to a respective outer layer.

45 Figure 2 shows schematically a device for making the films of the present invention.

A single melt stream, or multiple melt streams including a first melt stream of a blend of propylene polymer or copolymer, and ethylene copolymer, are extruded or coextruded and exit as an extrudate through an annular die 12 in a conventional manner. The extruded film is hot blown to form a blown bubble 14.

50 Air cooling ring 16 positioned circumferentially around the blown bubble at the position shown cools the thermoplastic melt as it exits die 12.

An optional auxiliary chilling ring or rings 17 may also be positioned circumferentially around the blown bubble down stream from air cooling ring 16 to further chill the hot blown film.

The primary bubble 14 is melt oriented in both the machine and transverse directions. Various blow up ratios may be used, but preferably the primary bubble 14 is hot blown to a blow up ratio of between 1.5 and 8.0.

The primary bubble 14 is collapsed at pinch rolls 21.

To assist in this process, guide plates 18 are positioned at the extremities of the blown bubble 14.

The preferred process for carrying out the present invention permits the bubble to be immediately reinflated, after

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cooling, into the secondary bubble 20 and then expanded to impart orientation of the material in primarily the transverse direction, primarily the longitudinal direction, or in both the transverse and longitudinal directions. This "flexibility" in the preferred process permits films of the invention to be produced which are oriented primarily in one direction (mono-axially oriented films) or films which are oriented in both the longitudinal and transverse directions (biaxially oriented films).

The collapsed bubble is reinflated in a blown bubble process to stretch orient the blown and collapsed film. This is done in a conventional manner by trapping air or other hot gas within the secondary bubble 20 so that the material stretches at its orientation temperature transversely to impart further orientation of the material in the transverse direction. The secondary bubble 20 is collapsed at a second set of pinch rolls 22. A second set of guide plates 24 may be employed to assist in the collapsing process.

The second set of pinch rolls 22 is rotated at a speed faster than the first set of pinch rolls 21 if it is desired to impart stretch orientation in the machine or longitudinal direction to the thermoplastic material.

The recollapsed bubble 20 then passes from the second set of pinch rolls 22 to take up roll 26.

The take up roll 26 may be a mill log which can be immediately stored or shipped to a distributor or customer, or may be stored for further processing such as slitting into single wound film, machine or natural center fold film. Thus, as used herein the take up roll 26 represents any further processing, storage, or further modification of the double wound, collapsed film once it exits the second set of pinch rolls 22, and is used herein to denote any of these possible further processing steps.

It is preferred that a reservoir 28 of heated fluid be disposed at the lower end of primary bubble 14 in such a way that the collapsing material drawn through the primary set of pinch rolls 21 will pass in communication with the heated fluid. In this manner, the film is more uniformly heated and temperature control can be achieved. Thickened tape edges can be substantially avoided by such means.

Although the heated fluid of reservoir 28 is preferably hot water, other media may be used if temperatures above the 100°C (212°F) limit of hot water are desired. For example propylene glycol (a food approved material), hot oil or hot emulsions may be used: One skilled in the art will understand that the exact nature of the heated fluid is not as critical as its effectiveness in helping to uniformly heat the collapsing bubble 14 as it is drawn through pinch rolls 21, and to uniformly heat the collapsing bubble 14 to a temperature above its orientation temperature.

The heated fluid may also be an "active" substance which not only reheats the surrounding film, but also actually coats the interior of the bubble as it passes over the reservoir. An example is a hot wax or other functional coating.

The heated fluid may be recirculated from the reservoir through a heating means 30 by means of conduits 32 or other suitable transfer means. Using the reservoir 28 of heated fluid, the types of materials which may be effectively used in the present process and device are increased.

Many different film constructions can be made using this process, including monolayer and multilayer films, especially those using the inventive blend compositions.

Biaxially oriented films of the present invention are useful in overwrap applications for overwrapping retail cuts of meat and non-food products.

Monoaxially oriented films are useful in shrink label applications for producing labels for vessels such as bottles and cans.

The term "monoaxially oriented" is used herein to mean films oriented primarily in the longitudinal direction. However, some incidental orientation can be present in the transverse direction, and this is sometimes desirable to help the film to grip a container or vessel after heat shrinking and to reduce the incidence of wrinkles in the final label. The term can also be used to refer to films oriented primarily in the transverse direction, with or without some incidental orientation in the longitudinal direction.

The invention may be further understood by reference to the examples which follow.

The examples below list preferred commercially available resins.

The resins used in these examples, and others useful in the invention, are identified in Table 1.

TABLE 1

RESIN	COMMERCIAL NAME	DESCRIPTION	COMPANY
SBC ₁	KR-10	STYRENE BUTADIENE COPOLYMER	PHILLIPS
SBC ₂	KK-36	STYRENE BUTADIENE COPOLYMER WITH FATTY FOOD COMPLIANCE	Phillips
EVA ₁	ELVAX 3182	EVA (28% VA)	DU PONT
EVA ₂	ELVAX 3165	EVA (18%VA)	DU PONT
EVA ₃	3170	EVA (18% VA)	DU PONT

Continuation of the Table on the next page

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TABLE 1 (continued)

RESIN	COMMERCIAL NAME	DESCRIPTION	COMPANY
VLDPE ₁	XU 61509.32	VERY LOW DENSITY POLYETHYLENE DENSITY = .911 grams/cc	DOW
VLDPE ₂	DEFD 1161	VERY LOW DENSITY POLYETHYLENE	UNION CARBIDE
VLDPE ₃	TAFMER 0680	VERY LOW DENSITY POLYETHYLENE DENSITY = .88 grams/cc	MITSUI
VLDPE ₄	1015	VERY LOW DENSITY POLYETHYLENE DENSITY = .900 grams/cc	UNION CARBIDE
PP ₁	8473	EPC	FINA
PP ₂	WRD5-981	POLYPROPYLENE	SHELL
PL ₁	22-164	50% POLYISOBUTYLENE IN LLDPE	SANTECH

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Example 1

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VLDPE₄ alone, and pellet blends with PP₁, were extruded at 260°C (500°F) barrel temperature on a 19.0 mm (3/4) inch extruder (Brabender) and blown into 50.8 µm (2 mil) thick film from a 25.4 mm (1 inch) annular die set at 232°C (450°F) with a blow-up ratio of 2.8:1.

The 50.8 µm (2 mil) films were then oriented into film using a hat tester on the following day. The results are shown below in Table 2.

Table 2

Composition	Orientation Temperature	Results
100% VLDPE ₄ *	99°C (210°F)	clear film
80% VLDPE ₄ + 20% PP ₁	100°C (212°F)	clear film
60% VLDPE ₄ + 40% PP ₁	107°C (225°F)	clear film
40% VLDPE ₄ + 60% PP ₁	107°C (225°F)	clear film
20% VLDPE ₄ + 80% PP ₁	107°C (225°F)	couldn't orient due to improper mixing (gels)

* comparison

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Double wound film (102 µm/4mils thick) of both 100% VLDPE₄, and the blend of 80% VLDPE₄ and 20% PP₁, were oriented on a hat tester (parallel orientation) at 99°C (210°F). A hat tester is a device for blow-orienting laboratory film samples. A film sample, having a size of about 102x102 mm (4 inches by 4 inches), is clamped over an orifice situated in a horizontal table. An overhead radiant heater heats the film to a predetermined orientation temperature. Then, air is blown upwardly through the orifice to create an oriented hemispherical shape ("hat") in the film. In each case, the resulting hat was ply separated after orientation into two hats of oriented film.

Example 2

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Multiple oriented hat samples for each of the compositions of Table 1 were made by the procedure described in Example 2. These hats were about 5.1 µm (.20 mils) thick. A styrofoam disc with a diameter of 66 mm (2.6 inches), and a 500 gram weight, were inserted into the cavity of each hat.

These hats were evaluated on a hot pad sealer to determine their burn-out threshold. The multiple hat samples for each composition, with the disc and weight therein, were each placed in turn on a hot pad preheated to different predetermined temperatures and left there for about 10 seconds. Each hat sample was evaluated for degree of burn-out. The aggregate results for each composition, are shown in Table 3.

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Table 3

Composition (% PP ₁)	Burn-out Threshold Temperatures
0*	110 to 116°C (230 to 240°F)
20	121 to 127°C (250 to 260°F)
40	138 to 143°C (280 to 290°F)
60	143 to 149°C (290 to 300°F)

* comparison

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Example 4

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A film having the construction SBC₁/EVA₁/80% VLDPE₄ + 20% PP₁/EVA₁/SBC₁ is produced by the process described above for Figure 2. Tubular film is hot blown, collapsed through a pair of pinch rolls and reinflated into a secondary bubble. The secondary bubble is stretched in the machine direction and in the transverse direction to produce a thin film.

The outer layers of SBC₁ each form about 15% of the final film gauge. The core layer of the blend of 80% VLDPE₁ and 20% PP₁ forms about 40% of the final film gauge by thickness. The intermediate adhesive layers of EVA₁ each comprise about 15% of the final film gauge.

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Example 5

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A film like that of Example 4 is made, by the same process, but having 20% VLDPE₄ + 80% PP₁ in the blend layer.

Additional films were produced by the process described above for Figure 2. These films are identified in Table 4 as Examples 6-8. The films of Examples 6-8 were oriented in the secondary bubble at a ratio of about 2.0:1 in each of the transverse and longitudinal directions.

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Table 4

<u>EXAMPLE</u>	<u>FILM STRUCTURE</u>	<u>BURNOUT TEMP</u>
6	SBC ₁ /EVA ₂ /80% VLDPE ₄ /EVA ₂ /SBC ₁ +20% PP ₂	138-149°C (280-300°F)
7	SBC ₁ /EVA ₂ /90% VLDPE ₄ /EVA ₂ /SBC ₁ +10% PP ₂	138-149°C (280-300°F)
8	SBC ₁ /EVA ₂ /70% VLDPE ₄ /EVA ₂ /SBC ₁ +30% PP ₂	138-149°C (280-300°F)

Additional films were made by standard blown film techniques, using about a 5:1 blow up ratio. These films are

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listed in Table 5 as Examples 9-16. The temperatures at which the films burned out in testing of the burn through resistance of the film are indicated in the right hand column of the table.

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Table 5

<u>EXAMPLE</u>	<u>FILM STRUCTURE</u>	<u>BURNOUT TEMP</u>
9 (Comparison) ¹	EVA ₂ /VLDPE ₄ /EVA ₂	127°C+ (260°F+)
10	EVA ₂ /VLDPE ₄ /90% VLDPE ₄ /VLDPE ₄ /EVA ₂ +10% PP ₂	138-143°C (280-290°F)
11	EVA ₂ /VLDPE ₄ /75% VLDPE ₄ /VLDPE ₄ /EVA ₂ +25% PP ₂	154-160°C (310-320°F)
12	EVA ₂ /VLDPE ₄ /50% VLDPE ₄ /VLDPE ₄ /EVA ₂ +50% PP ₂	160-166°C (320-330°F)
13	EVA ₂ /VLDPE ₄ /25% VLDPE ₄ /VLDPE ₄ /EVA ₂ +75% PP ₂	171°C (340°F)
14	SBC ₁ /EVA ₂ /80% VLDPE ₄ /EVA ₂ /SBC ₁ +10% PP ₂ +10% PP ₁	143-149°C (290-300°F)
15	SBC ₁ /EVA ₂ /VLDPE ₄ /50% VLDPE ₄ /VLDPE ₄ /EVA ₂ /SBC ₁ +50% PP ₂	143-149°C (290-300°F)
16	75% SBC ₁ /EVA ₂ /VLDPE ₄ /50% VLDPE ₄ /VLDPE ₄ /EVA ₂ /75% SBC ₁ +25% VLDPE ₃ / +50% PP ₂ / +25% VLDPE ₃	143-149°C (290-300°F)

Films of the present invention can optionally be cross-linked. This can be done chemically or by the use of irradi-

ation.

Irradiation may be accomplished by the use of high energy electrons, ultra violet radiation, X-rays, gamma rays, beta particles, etc. Preferably, electrons are employed up to about 20 megarads (MR) dosage level. The irradiation source can be any electron beam generator operating in a range of about 150 kilovolts to about 6 megavolts with a power output capable of supplying the desired dosage. The voltage can be adjusted to appropriate levels which may be for example 1,000,000 or 2,000,000 or 3,000,000 or 6,000,000 or higher or lower. Many apparatus for irradiating films are known to those of skill in the art. The irradiation is usually carried out at a dosage up to about 20 MR, typically between about 1 MR and about 20 MR, with a preferred dosage range of about 2 MR to about 12 MR. Irradiation can be carried out conveniently at room temperature, although higher and lower temperatures, for example, 0°C to 60°C may be employed.

For example, in an alternative embodiment, a single layer of said blend of propylene polymer or copolymer, and VLDPE can be adhered, either directly, by means of a polymeric adhesive layer, or by conventional lamination adhesives to a single layer of a sealable polymeric material by one of the methods disclosed herein, to produce a film with a preferred thickness of less than about 25.4 µm (1 mil). Thus, both asymmetric and symmetric two, three, four, five, six, and seven layer structures can be made. Additional layers can be added to these structures to meet specific end use requirements, such as toughness, and barrier properties.

Claims

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1. A multilayer film comprising:

(a) a first layer comprising a blend of propylene homopolymer or copolymer, and very low density polyethylene, wherein the very low density polyethylene has a melt index before blending of no more than 10 grams/10 minutes measured according to ASTM D 1238 at condition 190/21.601, and a flow rate ratio ($I_{21}/I_{2,1}$) before blending of at least 40, said ratio being derived by dividing the flow rate at condition 190/21.6 by the flow rate at condition 190/2.16, measured according to ASTM D 1238, and
(b) an outer sealable layer.

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2. A film according to claim 1 wherein the first layer comprises a blend of from 20% to 80% propylene homopolymer or copolymer, and from 80% to 20% very low density polyethylene.

3. A film according to claim 2 wherein the first layer comprises a blend of from 30% to 70% propylene homopolymer or copolymer, and from 70% to 30% very low density polyethylene.

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4. A film according to claim 3, wherein the first layer comprises a blend of from 40% to 60% propylene homopolymer or copolymer, and 60% to 40% very low density polyethylene.

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5. A film according to claim 4 wherein the first layer comprises a blend of about 50% propylene homopolymer or copolymer, and about 50% very low density polyethylene.

6. A film according to any one of the preceding claims wherein the outer sealable layer forms less than about 8% of the total film thickness.

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7. A film according to any one of the preceding claims wherein the outer sealable layer is adhered directly to the first layer.

8. A film according to any one of the preceding claims wherein the outer sealable layer is adhered to the first layer by means of a polymeric adhesive disposed between the first and second layers.

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9. A film according to claim 8 which comprises:

(a) a core layer comprising said blend of propylene homopolymer or copolymer and very low density polyethylene;

(b) two outer layers each comprising a sealable polymeric material; and

(c) two intermediate layers each bonding the core layer to a respective outer layer, and comprising a polymeric adhesive.

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10. A film according to claim 8, which comprises:

- (a) a core layer comprising said blend of propylene homopolymer or copolymer and very low density polyethylene;
- 5 (b) two interior layers, each layer bonded to an opposite side of the core layer, and comprising very low density polyethylene;
- (c) two outer layers each comprising a sealable polymeric material; and
- (d) two adhesive layers each bonding an interior layer to a respective outer layer.

10 11. A film according to claim 9 or 10 wherein the two outer layers each comprises from 0.1% to 10% by weight of each outer layer, of plasticiser.

12. A film according to any one of claims 9, 10 or 11 wherein the two outer layers each have a thickness of less than 100 μm (.04 mils).

15 13. A film according to any one of claims 9 to 12 wherein the two outer layers each comprise less than 4% of the total film thickness.

14. A film according to any one of claims 9 to 13 wherein the adhesive or intermediate layers comprise an olefin polymer or olefin copolymer with adhesive properties.

15 15. A film according to any one of claims 9 to 14 wherein the adhesive or intermediate layers comprise ethylene vinyl acetate copolymer.

25 16. A film according to any one of the preceding claims wherein the outer layer or layers comprise a sealable polymeric material which is an olefin polymer, olefin copolymer, styrenic polymer, or styrenic copolymer.

17. A film according to any one of the preceding claims wherein at least one layer of the film is crosslinked.

30 18. A method of making a polymeric film which comprises:

- (a) coextruding a first melt stream of a blend of propylene polymer or copolymer, and very low density polyethylene, wherein the very low density polyethylene has a melt index before blending of no more than 10 grams/10 minutes measured according to ASTM D 1238 at condition 190/21.601 and a flow rate ratio ($I_{21}/I_{2,1}$) before blending of at least 40, said ratio being derived by dividing the flow rate at condition 190/21.6 by the flow rate at condition 190/2.16, measured according to ASTM D 1238, and a second melt stream of a sealable polymeric material;
- 35 (b) extruding the melt streams through a tubular die;
- (c) hot blowing the extruded film;
- 40 (d) heating the hot blown film to a temperature above its orientation temperature;
- (e) directing the heated film through a first set of pinch rolls;
- (f) reinflating the hot blown film by a blown bubble process; and
- (g) collapsing the reinflated film through a second set of pinch rolls.

45 19. A method according to claim 18 which comprises in step a) and b)

- a) coextruding a first melt stream of said blend of propylene polymer or copolymer, and very low density polyethylene, a second and third melt streams of a polymeric adhesive, and fourth and fifth melt streams of a sealable polymeric material; and
- 50 b) extruding the melt streams through an annular die such that the first melt stream forms the central layer of the coextrudate, and the fourth and fifth melt streams form the outermost surfaces of the coextrudate.

Patentansprüche

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1. Mehrschichtenfolie, die

- (a) eine erste Schicht, die eine Mischung aus Propylenhomopolymer oder -copolymer und Polyethylen mit

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sehr niedriger Dichte umfaßt, wobei das Polyethylen mit sehr niedriger Dichte vor dem Mischen einen nach ASTM D 1238 bei Bedingung 190/21,601 gemessenen Schmelzindex von nicht mehr als 10 g/10 Minuten und ein Fließgeschwindigkeitsverhältnis ($I_{2,1}/I_{2,1}$) vor dem Mischen von mindestens 40 aufweist, wobei dieses Verhältnis erhalten wird, indem die nach ASTM D 1238 bei Bedingung 190/21,6 gemessene Fließgeschwindigkeit durch die nach ASTM D 1238 bei Bedingung 190/2,16 gemessene Fließgeschwindigkeit geteilt wird, und

(b) eine versiegelbare Außenschicht umfaßt.

2. Folie nach Anspruch 1, bei der die erste Schicht eine Mischung aus 20 % bis 80 % Propylenhomopolymer oder -copolymer und 80 % bis 20 % Polyethylen mit sehr niedriger Dichte umfaßt.

3. Folie nach Anspruch 2, bei der die erste Schicht eine Mischung aus 30 % bis 70 % Propylenhomopolymer oder -copolymer und 70 % bis 30 % Polyethylen mit sehr niedriger Dichte umfaßt.

4. Folie nach Anspruch 3, bei der die erste Schicht eine Mischung aus 40 % bis 60 % Propylenhomopolymer oder -copolymer und 60 % bis 40 % Polyethylen mit sehr niedriger Dichte umfaßt.

5. Folie nach Anspruch 4, bei der die erste Schicht eine Mischung aus etwa 50 % Propylenhomopolymer oder -copolymer und etwa 50 % Polyethylen mit sehr niedriger Dichte umfaßt.

6. Folie nach einem der vorhergehenden Ansprüche, bei der die versiegelbare Außenschicht weniger als etwa 8 % der gesamten Dicke der Folie ausmacht.

7. Folie nach einem der vorhergehenden Ansprüche, bei der die versiegelbare Außenschicht direkt an die erste Schicht geklebt ist.

8. Folie nach einem der vorhergehenden Ansprüche, bei der die versiegelbare Außenschicht mittels eines zwischen der ersten und der zweiten Schicht liegenden polymeren Klebstoffs an die erste Schicht geklebt ist.

9. Folie nach Anspruch 8, die

(a) eine Kernschicht, die die Mischung aus Propylenhomopolymer oder -copolymer und Polyethylen mit sehr niedriger Dichte umfaßt;

(b) zwei Außenschichten, die jeweils ein versiegelbares polymeres Material umfassen, und

(c) zwei Zwischenschichten umfaßt, die jeweils die Kernschicht an eine entsprechende Außenschicht binden und einen polymeren Klebstoff umfassen.

10. Folie nach Anspruch 8, die

(a) eine Kernschicht, die die Mischung aus Propylenhomopolymer oder -copolymer und Polyethylen mit sehr niedriger Dichte umfaßt;

(b) zwei Innenschichten, wobei jede Schicht an eine entgegengesetzte Seite der Kernschicht gebunden ist und Polyethylen mit sehr niedriger Dichte umfaßt;

(c) zwei Außenschichten, die jeweils ein versiegelbares polymeres Material umfassen; und

(d) zwei Klebeschichten umfaßt, die jeweils die Innenschicht an eine entsprechende Außenschicht binden.

11. Folie nach Anspruch 9 oder 10, bei der die beiden Außenschichten jeweils 0,1 bis 10 Gew.% Weichmacher enthalten, bezogen auf die jeweilige Außenschicht.

12. Folie nach einem der Ansprüche 9, 10 oder 11, bei der die beiden Außenschichten jeweils eine Dicke von weniger als 10 µm (0,04 mil) aufweisen.

13. Folie nach einem der Ansprüche 9 bis 12, bei der die beiden Außenschichten jeweils weniger als 4 % der gesamten Dicke der Folie ausmachen.

14. Folie nach einem der Ansprüche 9 bis 13, bei der die Klebe- oder Zwischenschichten ein Olefinpolymer oder Olefincopolymer mit Klebeeigenschaften umfassen.

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15. Folie nach einem der Ansprüche 9 bis 14, bei der die Klebe- oder Zwischenschichten Ethylen/Vinylacetat-Copolymer umfassen.

5 16. Folie nach einem der vorhergehenden Ansprüche, bei der die Außenschicht oder die Außenschichten ein versiegelbares polymeres Material umfassen, das ein Olefinpolymer, Olefincopolymer, von Styrol abgeleitetes Polymer oder von Styrol abgeleitetes Copolymer ist.

10 17. Folie nach einem der vorhergehenden Ansprüche, bei der mindestens eine Schicht der Folie vernetzt ist.

18. Verfahren zur Herstellung einer Polymerfolie, bei dem

15 (a) ein erster Schmelzestrom aus einer Mischung aus Propylenpolymer oder -copolymer und Polyethylen mit sehr niedriger Dichte, wobei das Polyethylen mit sehr niedriger Dichte vor dem Mischen einen nach ASTM D 1238 bei Bedingung 190/21,601 gemessenen Schmelzindex von nicht mehr als 10 g/10 Minuten und ein Fließgeschwindigkeitsverhältnis ($I_{21}/I_{2,1}$) vor dem Mischen von mindestens 40 aufweist, wobei das Verhältnis erhalten wird, indem die nach ASTM D 1238 bei Bedingung 190/21,6 gemessene Fließgeschwindigkeit durch die nach ASTM D 1238 bei Bedingung 190/2,16 gemessene Fließgeschwindigkeit geteilt wird, und ein zweiter Schmelzestrom aus einem versiegelbaren polymeren Material coextrudiert werden;

20 (b) die Schmelzeströme durch eine Ringdüse extrudiert werden;

25 (c) die extrudierte Folie warmgeblasen wird;

30 (d) die warmgeblasene Folie auf eine Temperatur oberhalb ihrer Orientierungstemperatur erwärmt wird;

35 (e) die erwärmte Folie durch einen ersten Satz von Quetschwalzen gelenkt wird;

35 (f) die warmgeblasene Folie mittels eines "blown-bubble"-Verfahrens (Verfahren mit geblasenen Blasen) erneut aufgeblasen wird; und

35 (g) die erneut aufgeblasene Folie durch einen zweiten Satz von Quetschwalzen zusammenfallen gelassen wird.

19. Verfahren nach Anspruch 18, bei dem in den Stufen (a) und (b)

30 (a) ein erster Schmelzestrom dieser Mischung aus Propylenpolymer oder -copolymer und Polyethylen mit sehr niedriger Dichte, ein zweiter und dritter Schmelzestrom aus einem polymeren Klebstoff und vierte und fünfte Schmelzeströme aus einem versiegelbaren polymeren Material coextrudiert werden; und

35 (b) die Schmelzeströme durch eine Ringdüse extrudiert werden, so daß der erste Schmelzestrom die mittlere Schicht des Coextrudats bildet und der vierte und fünfte Schmelzestrom die am weitesten außen liegenden Oberflächen des Coextrudats bilden.

Revendications

40 1. Film multicouches comprenant :

45 (a) une première couche comprenant un mélange d'homopolymère ou copolymère de propylène, et de polyéthylène très faible densité, dans laquelle le polyéthylène très faible densité a un indice de fusion avant mélange de pas plus de 10 grammes/10 minutes mesuré selon la norme ASTM D 1238 pour la condition 190/21,601, et un rapport de vitesse d'écoulement ($I_{21}/I_{2,1}$) avant mélange d'au moins 40, ledit rapport résultant de la division de la vitesse d'écoulement pour la condition 190/21,6 par la vitesse d'écoulement pour la condition 190/2,16, mesuré selon la norme ASTM D 1238, et

50 (b) une couche externe scellable.

50 2. Film selon la revendication 1 dans lequel la première couche comprend un mélange de 20% à 80% d'homopolymère ou copolymère de propylène et de 80% à 20% de polyéthylène très faible densité.

55 3. Film selon la revendication 2 dans lequel la première couche comprend un mélange de 30% à 70% d'homopolymère ou copolymère de propylène, et de 70% à 30% de polyéthylène très faible densité.

55 4. Film selon la revendication 3, dans lequel la première couche comprend un mélange de 40% à 60% d'homopolymère ou copolymère de propylène, et de 60% à 40% de polyéthylène très faible densité.

5. Film selon la revendication 4, dans lequel la première couche comprend un mélange d'environ 50% d'homopolymère ou copolymère de propylène, et d'environ 50% de polyéthylène très faible densité.
- 5 6. Film selon l'une quelconque des revendications précédentes dans lequel la couche externe scellable forme moins d'environ 8% de l'épaisseur totale du film.
7. Film selon l'une quelconque des revendications précédentes dans lequel la couche externe scellable est adhérée directement sur la première couche.
- 10 8. Film selon l'une quelconque des revendications précédentes dans lequel la couche externe scellable est adhérée sur la première couche au moyen d'un adhésif polymère disposé entre les première et seconde couches.
9. Film selon la revendication 8, qui comprend :
 - 15 (a) une couche d'âme comprenant ledit mélange d'homopolymère ou copolymère de propylène et de polyéthylène très faible densité;
 - (b) deux couches externes, comprenant chacune un matériau polymère scellable;
 - (c) deux couches intermédiaires reliant chacune la couche d'âme à une couche externe respective, et comprenant un adhésif polymère.
- 20 10. Film selon la revendication 8, qui comprend :
 - (a) une couche d'âme comprenant ledit mélange d'homopolymère ou copolymère de propylène et de polyéthylène très faible densité;
 - 25 (b) deux couches intérieures, chaque couche étant reliée à un côté opposé de la couche d'âme, et comprenant du polyéthylène très faible densité;
 - (c) deux couches externes comprenant chacune un matériau polymère scellable; et
 - (d) deux couches adhésives reliant chacune une couche intérieure à une couche externe respective.
- 30 11. Film selon la revendication 9 ou 10, dans lequel les deux couches externes comprennent chacune de 0,1% à 10% en poids de chaque couche externe, de plastifiant.
12. Film selon l'une quelconque des revendications, 9, 10 et 11, dans lequel les deux couches externes possèdent chacune une épaisseur de moins de 100µm (0,04 mil).
- 35 13. Film selon l'une des revendications 9 à 12 dans lequel les deux couches externes comprennent chacune moins de 4% de l'épaisseur totale du film.
14. Film selon l'une des revendications 9 à 13 dans lequel les couches intermédiaires ou adhésives comprennent un polymère d'oléfine ou un copolymère d'oléfine avec des propriétés adhésives.
- 40 15. Film selon l'une des revendications 9 à 14 dans lequel les couches intermédiaires ou adhésives comprennent un copolymère d'éthylène vinyl acétate.
- 45 16. Film selon l'une des revendications précédentes dans lequel la ou les couches externes comprennent un matériau polymère scellable qui est un polymère d'oléfine, un copolymère d'oléfine, un polymère de styrène, ou un copolymère de styrène.
17. Film selon l'une des revendications précédentes dans lequel au moins une couche du film est réticulée.
- 50 18. Procédé de fabrication d'un film polymère qui consiste :
 - (a) à coextruder un premier courant de produit fondu consistant d'un mélange de polymère ou copolymère de propylène, et de polyéthylène très faible densité, dans lequel le polyéthylène très faible densité possède un indice de fusion avant mélange de pas plus de 10 grammes/10 minutes mesuré selon la norme ASTM D 1238 à la condition 190/21.601 et un rapport de vitesse d'écoulement ($I_{21}/I_{2,1}$) avant mélange d'au moins 40, ledit rapport résultant de la division de la vitesse d'écoulement à la condition 190/21.6 par la vitesse d'écoulement à la condition 190/2.16, mesuré selon la norme ASTM D 1238, et un deuxième courant de produit fondu d'un

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matériau polymère scellable;

(b) à extruder les courants de produit fondu à travers une filière tubulaire;

(c) à souffler à chaud le film extrudé;

(d) à chauffer le film soufflé à chaud à une température au-dessus de sa température d'orientation;

5 (e) à diriger le film chauffé au travers d'un premier jeu de rouleaux de pinçage;

(f) à regonfler le film soufflé à chaud à l'aide d'un procédé à bulle soufflée; et

(g) à affaisser le film regonflé par passage dans un second jeu de rouleaux de pinçage.

19. Procédé selon la revendication 18, qui consiste dans l'étape a) et l'étape b)

10 (a) à coextruder un premier courant de produit fondu dudit mélange de polymère ou copolymère de propylène, et de polyéthylène très faible densité, un deuxième et troisième courant de produit fondu d'un adhésif polymère, et un quatrième et cinquième courant de produit fondu d'un matériau polymère scellable; et

15 (b) à extruder les courants de produit fondu au travers d'une filière annulaire telle que le premier courant de produit fondu forme la couche centrale du coextrudat, et le quatrième et cinquième courants de produit fondu forment les surfaces les plus externes du coextrudat.

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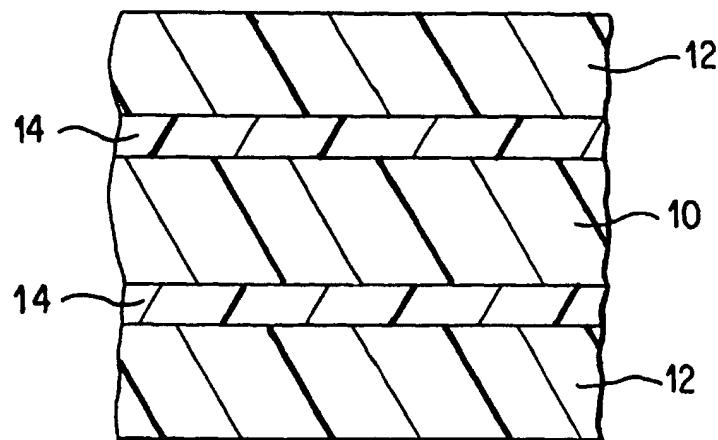


FIG. 1

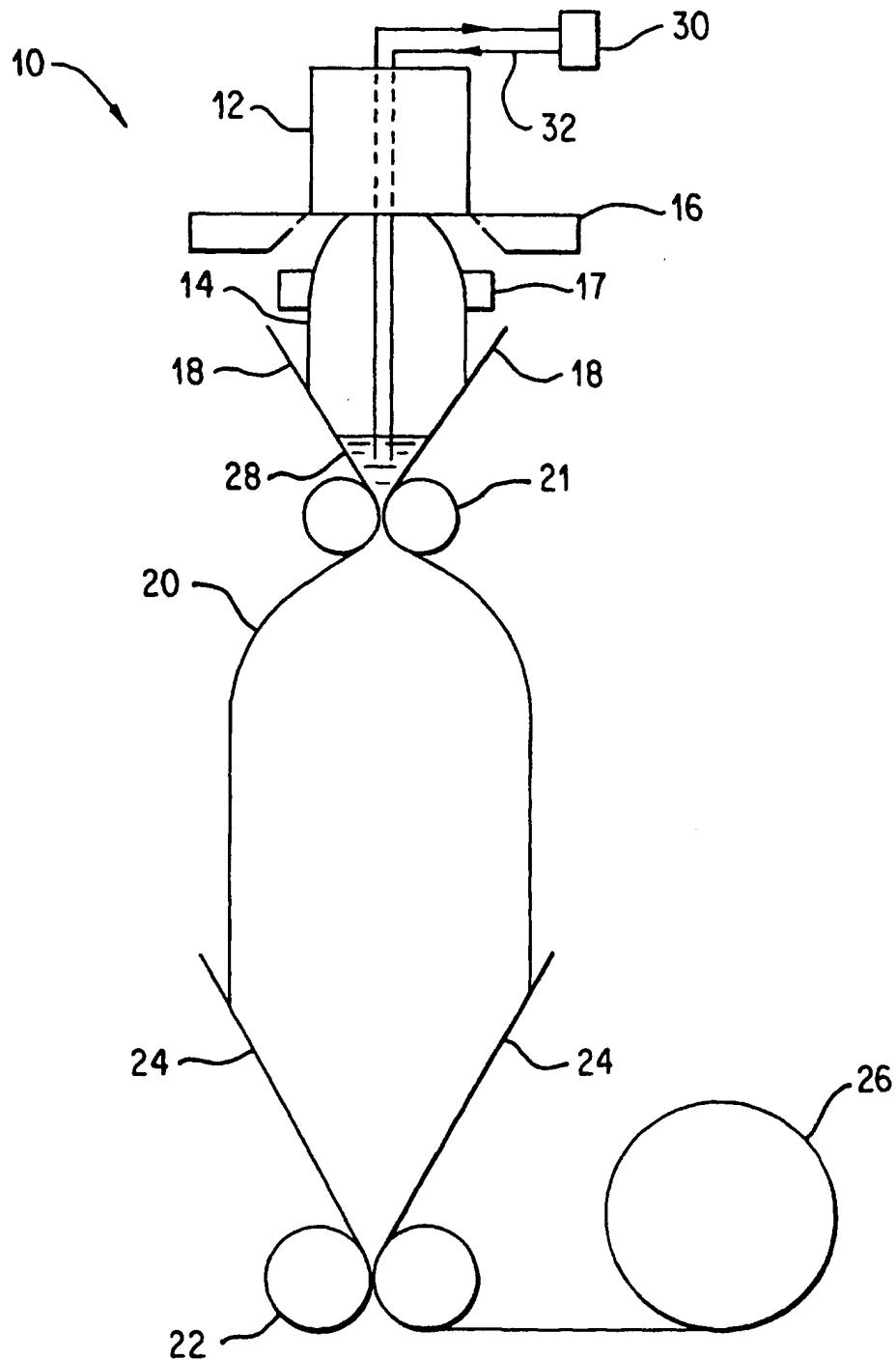


FIG. 2